

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS ON MIR SPACE STATION FINAL REPORT

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INTRODUCTION

The goal of this research was the characterization of volatile organic compounds (VOCs) in air samples from Mir Space Station using new technology based on ion trap mass spectrometry (ITMS). Twenty-four hour time-averaged samples were collected onto cartridges using the US Solid Sorbent Air Samples (SSAS). Grab samples were collected using US Grab Sample Containers (GSC). Samples were transferred from Mir via the Space Shuttle, forwarded to the Toxicology Laboratory at NASA Johnson Space Center (JSC) for analysis and sample subdivision, and then sent on to San Francisco State University (SFSU) for the purposes of this work. Samples were analyzed using a modified form of EPA-approved gas chromatography/mass spectrometry (GC/MS) methods [1] and an emerging technology hereinafter referred to as direct sampling ion trap mass spectrometry (DSITMS) [2-4]. Significant effort was put into the development, testing, and validation of DSITMS sample introduction systems, ionization techniques, and mass spectrometric methods for sensitive, selective, and near real-time monitoring of trace-level contaminants in air. The results of this research have provided detailed information on the types and concentrations of VOCs in the Mir environment. Moreover, the demonstration of new DSITMS technology and their comparison against proven methods has yielded valuable information on the feasibility of its use for monitoring air quality in advanced life support systems and other environments.

Hypotheses

The types and concentrations of VOCs in the Mir Station atmosphere are not well characterized. Detailed information on the types and concentrations of VOCs in the Mir Station atmosphere is required to assess the toxicological risks of long-term human exposure to this environment.

Detailed information on the types and concentrations of VOCs in the Mir Station atmosphere can be obtained through the use of the same proven methods employed for previous U.S. space missions. These methods, based on the use of both cartridges and grab samples for sampling, and GC/MS for analysis, represent the most reliable, cost-effective means for characterizing this environment.

New technology based on DSITMS shows excellent promise for on-line, real-time monitoring of VOCs. Demonstration of this technology on air samples collected from Mir Station can provide a means for intercomparison with conventional GC/MS methods and provide a measure of its potential for environmental health assessments and advanced life support applications.

Objectives of Investigation

The objectives of this investigation were threefold:

1. Characterize Mir Station atmosphere via proven sampling and analysis strategies.
2. Demonstrate the use of DSITMS for direct monitoring of VOCs in air samples collected from Mir Station.
3. Document the types and concentrations of VOCs on Mir Station and analyze results in collaboration with other science investigators to further the goals of the NASA Research Announcement (NRA).

Background/History

Palmer and the JSC Toxicology Lab signed a Memorandum of Understanding (MOU) that detailed the nature of their collaborative research on characterization of VOCs in Mir air samples. The JSC Toxicology Lab has extensive experience on space station air analysis and flown SSAS and GSC units on a variety of prior NASA missions ranging from the Apollo through the Shuttle programs [5-9]. Palmer and Belisle have additional experience analyzing for VOCs in air samples collected in various locations in the San Francisco Bay Area [10-11], boreal ecosystems [12], and bioregenerative life support chambers [13,14]. Palmer's previous mission experience includes a set of "practice" samples from the Mir 19 mission [15]. These samples enabled the testing of analytical methods and instrumentation, and the garnering of practical experience on space station air samples. Analytical results on these samples, that is compounds tentatively identified and their concentrations, were reviewed with researchers at the JSC Toxicology Lab and generally showed good agreement. This report includes data from Mir missions 21, 22, 23, and 24. It includes data from previous reports filed by the investigators on the Mir 21 [16] and 22 [17] missions, and data on samples from the Mir 23 and 24 missions which have not been included in any prior reports to date.

METHODS/RESEARCH OPERATIONS

Functional Objectives

FO1. Collect instantaneous air samples using GSCs.

FO2. Collect 24-hour time-averaged samples using the SSAS unit.

A summary of the functional objectives is provided in Table 1. This represents a compilation of each sampling event, sampling method, sampling date, identification code for Mir missions 21, 22, 23, and 24.

Hardware Items

HW1. GSC - Grab sample container capable of collecting an instantaneous air sample.

HW2. SSAS - Solid Sorbent Air Sampler capable of collecting up to 7 time-averaged air samples.

Note that detailed information on these hardware items, schematics, and dimensions may be obtained from the JSC Toxicology Lab.

Method/Protocol

Specific methods to delineate the steps involved with unstowing the sampling devices, collecting air samples, restowing the sampling devices, and transferring the sampling devices to and from the Shuttle have been documented by the JSC Toxicology Lab. The methods used to collect air samples using these devices are briefly described here. For GSCs, this involves recording the date, time, and location; opening a valve on the GSC to begin collection of the air sample; and then closing the valve once the GSC pressure has reached ambient pressure. For the SSAS unit, this involves recording the date, time, and location, switching the valve on the SSAS unit from a "park" location to one of the 7 sampling tube locations, and turning on the sampling pump to begin collection. After the desired sampling interval is complete (usually ~24 hours), the date and time are again recorded, the sampling pump turned off, and the valve is switched back to the "park" location.

RESULTS

List of Pre-, In-, and Post-Flight Anomalies

Samples taken near the end of the Mir-23 mission were lost when Spektr decompressed. No samples were taken at the beginning of the Mir 24 mission as new GSC and SSAS units were not available until the arrival of STS-86. One of the samples from the Mir 21 mission (AA01336) was not analyzed, as the GSC valve was left open and the sample was subsequently lost.

Completeness/Quality of Data

GC/MS analyses on first subset of samples from the Mir 21 mission (AA01241, AA01243, UNK1, UNK2) were performed in Palmer's labs at San Francisco State University, as Belisle's instrumentation had not yet been installed and run through the appropriate performance tests. GC/MS analyses on the remaining samples from the Mir 21 mission (AA01336, AA01339, AA01353, AA01356) and Mir 22 and 23 missions were performed in Belisle's labs. Samples from the Mir 24 mission were not analyzed via GC/MS so as to preserve the samples for DSITMS analyses. As will be shown later on in this report, GC/MS results show the consistent detection of several chlorinated, fluorinated, aromatic, and silyated hydrocarbons.

DSITMS analyses were not performed on the first subset of samples from the Mir 21 mission (AA01241, AA01243, UNK1, UNK2), as the DSITMS instrumentation was not yet fully tested and operational. DSITMS analyses were performed on samples from the Mir 22, 23, and 24 missions and are reported here. As will be discussed in more detail later, the results from the DSITMS analyses are more qualitative than quantitative due to several factors. As will be shown later on in this report, DSITMS successfully identified the few fluorinated, aromatic, and silyated hydrocarbons which were present in the samples at concentrations greater than the 50 ppb detection limit of this technique.

It must be stressed that the reader should exercise care in interpreting the data in this report, as there are numerous sources of error inherent to these experiments. The major source of error stems from the long time period between sampling and analysis, which in many cases was more than one year. This was unavoidable due to the length of time required for the samples to be returned to Earth, analyzed by the JSC Toxicology Lab, and then forwarded on the principal investigator and co-investigator. The stability of VOCs in canisters over these time periods is unknown, and this most certainly will affect the accuracy of the results reported here.

A second source of error is the inherent variability of the air samples themselves. The composition of a particular air sample is a function of the time and location of the sampling, as well as the proximity of pollutant sources and their relative strengths. The samples from this study were collected at several different locations on Mir, and the air composition on Mir is most certainly not homogeneous. VOC concentrations have significant uncertainties associated with them, as evidenced by anyone who has watched the smoke from a candle disperse after it has been blown out.

A third source of error involves the two different sampling methods, which are different in both the types of VOCs targeted and the duration of the sampling period. GSCs can be used to sample highly volatile species such as fluorocarbons and chlorofluorocarbons, whereas these same compounds are not efficiently trapped on the SSAS device. GSCs are used to collect instantaneous samples while the SSAS device is typically used to collect samples over a 24-hour time period.

A fourth source of error is the analytical instrumentation. The use of air concentrators for GC/MS analyses is fraught with potential problems that include carryover from previous samples, contamination in the system, and leaks of lab air into the system. Implementation of even the best QA/QC procedures cannot guarantee that such problems will occur.

A fifth source of error involves the methods and the personnel involved in implementing the analyses. The samples were handled by numerous individuals on Mir, the Shuttle, the JSC toxicology Lab, Palmer's labs, and Warren Belisle's labs. The GC/MS methods employed at the JSC Toxicology Lab, Palmer's labs, and Warren Belisle's labs were slightly different. Additionally, the specific method parameters and even the target compounds varied within each lab from one mission to the next. Finally, gas standards for each and every VOC identified in the samples were not always readily available. In such cases, quantitation was performed indirectly and resulted in significantly higher uncertainties in the computed concentrations.

Those uninitiated to the hazards and pitfalls of air analyses should note that even the most rigorous QA/QC procedures for analysis of air toxics via GC/MS provide accuracy and precision approaching 10-20% at best. Lastly, it should be pointed out that there are even larger uncertainties in the space maximum allowable concentrations (SMACs) postulated for each VOC [18,19], and that these limits are only guidelines and do not take into account an individual's age, sex, race, physiology, and health.

DISCUSSION

Status of Data Analysis

Analysis of the samples via GC/MS and DSITMS methods [1] was successful. GC/MS results from Mir 21 and 22 were previously documented elsewhere [16,17] and are reported here as well for completeness. Final reports for Mir missions 23 and 24 were not filed, and this report includes GC/MS results from Mir 23 and DSITMS results from Mir 22, 23, and 24.

Final Research Findings

Introduction

Two types of samples were collected from Mir station: grab samples using GSCs and time-averaged samples using the SSAS unit. Information describing where and when these samples were collected and how they were processed was provided by the JSC Toxicology Lab and is shown in Table 2.

Experimental

GC/MS Analyses: Mir samples and standards were analyzed using a modified form of the EPA TO-14 method [1]. The most salient experimental details on analytical methods employed are summarized here. Detailed information on preparing standards, tuning the GC/MS instrument, and quality assurance/quality control (QA/QC) procedures are beyond the scope of this report and are documented elsewhere [16,17,20].

An air concentrator was used to isolate the VOCs from the bulk of the air sample. Samples were pulled out of a stainless steel canister and passed through a cryogenically-cooled internal trap. VOCs were desorbed from this internal trap and cryofocused onto the head of the GC column. Injection was achieved by flash heating the head of the column. A gas chromatograph/ion trap mass spectrometer was used to separate and detect individual VOCs.

A number of QA/QC procedures were implemented for the GC/MS analyses. Blanks were analyzed to ensure that the sample path through both the air concentrator and GC/MS instrument were not contaminated and background ion counts were acceptable. Canisters used to prepare the working gas standards were cleaned with humidified, purified air and their cleanliness proofed by GC/MS analysis prior to use. Mass spectrometer response was tuned to meet EPA criteria for bromofluorobenzene. Identification of specific

VOCs in the Mir samples was achieved via a combination of both a retention time match to previously analyzed standards and library searching of experimental spectra against the NIST library of approximately 60,000 reference mass spectra. A Supelco TO-14 100 per-billion by volume (ppb) gas standard containing 37 common VOCs was used to prepare a series of working standards. Neat stock solutions were prepared and used to generate an additional series of working standards for additional target compounds as necessary. Five-point calibration curves were established for each target compound and internal standards were employed in standards and samples to correct for variations in instrument response (note that this was not the case for the GC/MS analyses performed in Palmer's labs). Special software was employed to automate VOC identification and quantitation. The results were entered into Microsoft Excel spreadsheets and VOC concentrations in the original Mir samples were computed using sample data provided by the JSC Toxicology Lab. Replicate sample analyses were performed on some of the samples due to limited sample volumes and the desire to perform subsequent DSITMS analyses.

DSITMS Analyses: Mir samples and standards were analyzed using a variation of a proposed EPA method [21,22]. Again, only the most salient experimental details are summarized here. More detailed information on the preparation of gas standards, tuning the ion trap instrument, and acquiring data for DSITMS analyses are beyond the scope of this report and are documented elsewhere [23-27].

The sample introduction system employed for these DSITMS analyses is referred to as the Real-Time Air Monitor (RTAM). This is a prototype inlet system developed by Scientific Instrument Services based on a design originated by researchers at Oak Ridge National Laboratories [28]. The RTAM mixes an air sample into a helium stream, and then passes the combined stream through an open-split interface prior to introduction into a Teledyne Discovery ion trap mass spectrometer. It should be noted that two different versions of the RTAM were used in this work: the older RTAM which used a single sample path and relatively high sample consumption rates [28], and the newer RTAM which used two sample paths and lower sample flowrates [29]. These old and new RTAM systems are shown in Figures 1 and 2, respectively. All experiments employed the ion trap in conventional MS scan mode to detect as many VOCs in the samples in a single acquisition. Although separate MS/MS scan functions would permit more selective detection and more accurate quantitation of individual VOCs, the limited sample volumes (often on the order of ~ 100 mL) and the RTAM's high rate of sample consumption (approximately 1 L/min) precluded their use here. A low mass cutoff of m/z 60 was employed to eject relatively large background ion signals below this value from the trap. A scan range of m/z 60 to 220 was used to detect major VOC ions expected to be present in these samples. The RTAM was operated in a continuous mode of operation, where the inlet was challenged with zero-grade air for 60 seconds followed by the sample or a gas standard.

QA/QC procedures were implemented insofar as the limited sample volumes and compromises inherent to these DSITMS analyses allowed. Samples were transferred into previously cleaned and proofed Tedlar bags just prior to analysis. Background-corrected mass spectra for each sample were obtained by subtracting an average background response when analyzing zero-grade air and helium from the average sample response. Replicates of each sample were not analyzed, as the RTAM performs continuous monitoring on each sample, and the results were hence computed from average responses of specific ions. The samples were analyzed in MS mode only, as there were insufficient sample volumes and ion intensities for more selective MS/MS analyses for specific target compounds. VOCs in each sample were tentatively identified by the presence of characteristic ions in MS mode. Intermediate gas standards were prepared in a static dilution bottles from neat liquids of the pure compound. Working gas standards were prepared in Tedlar bags via dilutions into known volumes with gas-tight syringes [23]. Four-point calibration curves were established for each VOC via working standards prepared and analyzed on the same day as the samples. In some cases, quantitation could not be performed due to the lack of gas standards, overlapping quantitation ions, and/or low ion intensities in the samples. Teledyne Discovery software was used for data analysis. Microsoft Excel was

used to generate calibration curves, compute standard deviations and least squares fits, and compute sample concentrations.

Results

GC/MS Analyses: Results from GC/MS analyses of air samples from the Mir 21-23 missions are shown in Tables 3-19. Concentrations in this report are given in units of mg/m^3 which are the standard units used by both the JSC Toxicology Lab and EPA for reported toxic air contaminant concentrations. There is a prodigious amount of data in these tables and some summarization is necessary to facilitate their interpretation. The reader is urged to note the caveats discussed in the section above on completeness/quality of data.

The target compounds for these analyses included VOCs in the TO-14 standard plus additional VOCs including fluorocarbons, terpenes, oxygenated hydrocarbons, and siloxanes that were identified in samples from prior Mir missions or suspected to be present in the samples. Many of the VOCs were not identified in any of the samples, some were only rarely identified, and fewer still were identified on a semi-consistent basis in most of the samples. This last category of VOCs can be roughly sorted into the categories of fluorocarbons, chlorofluorocarbons, aromatic hydrocarbons, biogenic hydrocarbons, and siloxanes. These VOCs and their concentrations are the focus of this discussion and their concentrations are summarized in Figures 3-14. These figures provide comparisons of these VOCs and their concentration determined in each sample. They are intentionally separated via sampling method (i.e., GSC or SSAS) due to the nature of the different VOCs targeted by these methods and their different sampling durations.

Two fluorocarbons were identified in the Mir samples: perfluoropropane (octafluoropropane) and perfluoro-1,3-dimethylcyclohexane. Data for these compounds are summarized in Figures 3 and 4. These compounds were detected at concentrations higher than any other VOC detected on Mir. Although no SMACs have been established for these compounds, it is assumed that like other fluorocarbons, such as those used in artificial blood, that they are nonreactive and nontoxic. Perfluoropropane and perfluoro-1,3-dimethylcyclohexane are most likely employed as coolants in the refrigeration/thermal control systems onboard Mir, and hence would be expected to be found in every sample analyzed. However, they are highly volatile and not easily trapped at the liquid nitrogen temperatures used in the air concentrators. This is reflected by the fact that these compounds were not detected in every sample, and the relatively high relative standard deviations (RSD) for these two compounds in the replicate analyses. Additionally, these compounds are not trapped efficiently on the SSAS device and most likely “breakthrough” the sample cartridge. This is evidenced by the concentrations on the SSAS device which are more than an order of magnitude lower than those found in the GSCs. Perfluoropropane was not included as a target or non target compound in some of the GC/MS analyses, and/or the experimental parameters associated with the air concentrator were not set properly, and hence this compound was not detected in every sample.

Several chlorofluorocarbons and chlorinated hydrocarbons were identified in several Mir samples, including dichlorodifluoromethane (CFC12), trichlorofluoromethane (CFC11), trichlorotrifluoromethane, and methylene chloride. Data for these compounds are summarized in Figures 5 and 6. These are relatively unreactive compounds that are ubiquitous on Earth, have relatively long atmospheric lifetimes, and may have been transported onboard Mir by repeated dockings of resupply vehicles. They may also have sources in the materials on Mir. As with the fluorocarbons, these compounds are highly volatile, not trapped efficiently on the SSAS device, and not easily trapped at the liquid nitrogen temperatures used in the air concentrators. Again, these compounds were not detected in every sample, and had relatively high relative standard deviations (RSD) in the replicate analyses. Once again, for GSC and SSAS samples collected on the same dates, chlorofluorocarbon concentrations track one another, indicating the reliability of the data even if the accuracy may be compromised.

The major aromatic hydrocarbons identified in the Mir samples included benzene, toluene, ethylbenzene, and xylenes (BTEX). Data for these compounds are summarized in Figures 7 and 8. These species are also ubiquitous on Earth, as they are a major component in gasoline and have long atmospheric lifetimes. They may have been transported onboard Mir by frequent dockings of resupply vehicles, or may have outgassed from materials on Mir. Toluene, ethylbenzene, and the xylene isomers were detected in every sample analyzed. Benzene was detected in only three samples, and it is interesting to note that these samples were collected shortly after the fire event on Mir, as it was most likely generated as a product of incomplete combustion. Several other possible products of incomplete combustion were also indicated in these same samples, including styrene and two nitrile species. Although benzene's peak concentration of 0.387 mg/m³ did not exceed the 7-day SMAC of 1.5 mg/m³ [18,19], it should be noted that concentrations of benzene in closer proximity to the shortly after the fire occurred may have been higher than this value reported for this individual sample. After the fire event, benzene concentrations dropped, indicating the capability of the trace contaminant removal system onboard Mir to remove this contaminant. Unlike the fluorocarbons and chlorofluorocarbons, the GSC and SSAS sampling devices provide comparable results, as shown by the similar concentrations found for samples collected on the same dates. Additionally, the RSDs were smaller for these compounds, indicating their stability in the sampling devices and smaller uncertainties in the analytical methods employed.

Several biogenic hydrocarbons were detected in some of the Mir samples. These include isoprene, terpenes, and 2-ethyl-1-hexenol. Data for the two most frequently identified biogenic hydrocarbons, limonene and 2-ethyl-1-hexenol, are shown in Figures 9 and 10. These compounds are known to be emitted by a variety of plant species. They may have been produced by one or more of the plant growth experiments or vegetable products on Mir, or may have been transported onboard by the resupply vehicles. It is interesting to note how the concentrations of these two species track one another, indicating a common source. It should be noted that the concentrations on the SSAS samples are lower than those found in the GSC samples collected on the same date. The instability of these reactive hydrocarbons on sorbent traps and in the presence of ozone has been well established in the atmospheric chemistry community, indicating that GSC and not SSAS devices should be relied upon to establish more accurate concentrations of these species.

Two siloxane compounds were identified on Mir: hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane. Data for these two compounds are summarized in Figures 11 and 12. With the exception of the two fluorocarbons discussed above, these two siloxanes were present at concentrations higher than all other VOCs detected on Mir. A review of the literature yielded very little detailed information on gaseous siloxane contaminants other than to note their ubiquitous nature. A Boeing publication states that *"these compounds were observed consistently in samples but not in system blanks analyzed between sample runs,"* and suggests a *"common system source"* for these compounds [30]. Our results cast doubt on this hypothesis and further studies were conducted in an attempt to elucidate possible sources of these siloxane contaminants.

The two most likely system sources include siloxane contamination in the air concentrator and siloxane bleed off of the GC column. The air concentrator was ruled out as a possible source for siloxane contamination, as neither hexamethylcyclotrisiloxane nor octamethylcyclotetrasiloxane were detected at significant levels in any of the system blanks and gas standards analyzed. Although the GC columns used in this work are constructed from siloxane polymers, the siloxane bleed off these columns gives chromatographic and mass spectral signatures that are distinctly different from Mir data [31]. Since our results showed the presence of siloxanes in the samples, this would indicate that these compounds are indeed present on Mir and neither an artifact of the method nor a result of contamination in the analytical system.

Polydimethylsiloxane (PDMS) polymers are used in a variety of commercial products including silicone-based sealants, anti-perspirants, and adhesive tapes. A sample of each of these products was selected as a potential source for siloxane contaminants on Mir, especially given the use for sealants in creating airtight seals, anti-perspirants by the cosmonauts and astronauts, and adhesive tape for labeling experiments and other items on Mir. Indeed, it should be noted that the GSC and SSAS devices themselves were labeled with masking tape, which was used to record sample information.

Several outgassing studies on these products were performed in an attempt to elucidate likely sources for these compounds on Mir [32,33]. This involved dosing small quantities of each product into pre-cleaned and proofed Tedlar bags. The bags were then filled to volume with “zero” grade air. The sealant and anti-perspirant samples were diluted 1000-fold by transferring 10 mL aliquots from the bags containing the products and diluting to 10 L with zero air in new pre-cleaned and proofed bags. 50-mL aliquots of the product samples were analyzed regularly over a 3-week period. Gas standards of both hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane were prepared and analyzed on the same dates as the samples. A constant volume of difluorobenzene (DFB) was added to both the samples and the standards for use as an internal standard in quantitation.

Results from these studies showed that sealant, anti-perspirant, masking tape, and scotch tape all emit these two siloxane compounds. The sealant and anti-perspirant outgassing studies showed part-per-million (ppm) levels of the hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane were generated as offgases, while the two tape samples generated low part-per-billion (ppb) levels of these same compounds. A comparison of the levels of siloxanes generated by these samples to those found on Mir is provided in Figure 15. The data indicate that the siloxane contaminants found on Mir can most likely be attributed to emissions from sealants and/or antiperspirants. Possible chemical mechanisms responsible for generation of these two siloxanes from the PDMS polymers present in the sealants and anti-perspirants are illustrated in Figure 16.

Lastly, d5-chlorobenzene was identified in most of the Mir samples. Data for this compound is summarized in Figures 13 and 14. As this is not a common contaminant, it is most likely that this species was introduced into the sampling devices prior to their transport to Mir as a surrogate standard. This enables determination of percent recovery, which is useful for QA/QC purposes to determine if the sampling device’s integrity has been maintained. Although it is assumed that each sampling device would be dosed with nearly identical amounts of d5-chlorobenzene, this is not evident from the data represented in the figures. Once again, the caveats pointed out above in the section on completeness/quality of data should be kept in mind. As no information was provided to the investigators as to the actual concentration of this surrogate standard, any further interpretation on the percent recovery of the analytical method employed is relegated to the JSC Toxicology Lab.

It should be noted that for GSC and SSAS samples collected on the same dates, concentrations of the individual compounds track one another, indicating the reliability of the methods to illustrate trends in concentrations regardless of the accuracy of individual measurements. Finally, it should be pointed out that all VOC concentrations were below their SMACs, most by more than 2-3 orders of magnitude, indicating the air quality onboard Mir was within specifications.

DSITMS Analyses: Several excellent descriptions and reviews of the DSITMS technique are reported in the literature [2-4]. Some of the results from this investigation on DSITMS analyses of Mir samples have been reported elsewhere [17,34,35]. This report provides the most complete review to date on the application of DSITMS to Mir sample analyses and its suitability for life support monitoring applications.

The following points should be noted prior to discussion of results from the DSITMS analyses.

1. VOC concentrations in the Mir samples were very low to begin with. The highest concentration VOC detected via GC/MS analyses was perfluoro-1,3-dimethyl-cyclohexane at approximately 12 mg/m³ in Mir 22 sample AA01467. This concentration is equivalent to 730 ppb.
2. The samples were subjected to two repressurizations (and hence dilutions) subsequent to successive GC/MS analyses at the JSC Toxicology Lab and NASA Ames Research Center. Hence, the VOC concentrations in *the samples subjected to DSITMS analyses* were lower than the VOC concentrations in *the original Mir samples*. Following up on GC/MS data in the example given above and factoring in the two dilution factors, the concentration of perfluoro-1,3-dimethyl-cyclohexane in sample AA01467 taken for DSITMS analysis is roughly 160 ppb.
3. The DSITMS detection limits were on the order of 10-50 ppb, which in combination with the two factors above, limited the scope of the DSITMS analyses to the few VOCs which were present above these concentrations in *the samples subjected to DSITMS analyses*.
4. The sample volumes available for analysis were relatively small. The GSCs used for storing both the GSC and SSAS samples were 350 mL in volume. Even when pressurized to their maximum safe limit of approximately 3 times ambient pressure (3 atm or 42 psia), this only provided approximately 750 mL of sample in a Tedlar bag when the canister was opened.
5. The DSITMS sample consumption rates were relatively large (~1 L/min) so as to provide fast response times and minimal carryover. This, in combination with the small sample volumes as discussed above, limited the duration and number of experiments that could be performed on each sample. Hence, nearly all of the DSITMS analyses used MS scan mode to enable detection of as many VOCs as possible in one analysis.

An illustration of how these factors collectively limit the scope of the DSITMS analyses is provided in Figure 17. This shows a plot of SMACs, average Mir concentrations, and average Mir sample concentrations for several VOCs. The first 6 VOCs are present at concentrations higher than nearly every other VOC detected on Mir, and the figure hence shows that their concentrations are at or below the DSITMS detection limits due to the low initial concentration on Mir and the sample repressurizations. On a more positive note, it should be stated that DSITMS detection limits meet the application requirements, which are detection of VOCs at approximately 1/10th of their SMAC levels. Even benzene, one of the acutely toxic VOCs, has a required detection limit which is slightly higher than 50 ppb, indicating that this DSITMS can meet the desired sensitivity criteria. It should also be noted the units reported here are ppb, mainly for the purposes of simplicity as the gas standards were prepared in these units, and due to the fact that such units are independent of temperature and pressure (which cannot be said for the more commonly employed units of mg/m³).

Data from the DSITMS analyses of Mir sample analyses are summarized in Tables 20-35. Some discussion of the format and content of these tables is appropriate here prior to a detailed discussion of the results. The tables list the major quantitation or “quan” ions observed in the mass spectra of gas standards of each tentatively identified VOC, or library spectra when gas standards and experimental spectra were not available. The tables also list the ions which were actually observed in the mass spectra of the Mir samples. Compounds were tentatively identified in the Mir samples when one or more of the quan ions from the experimental or library mass spectra were observed in the sample spectra. Although the use of MS/MS would enable more conclusive identification of each VOC, the small sample volumes precluded the execution of such experiments as discussed above. Although it is possible to obtain erroneous results from the use of MS scan modes for identifying specific VOCs in complex mixtures (i.e., false positives and false negatives), the use of DSITMS to screen for target compounds in well-characterized samples is accepted [2-4,21] and the results from prior GC/MS analyses of the same samples were used to facilitate interpretation of the DSITMS data. It should be noted that the tables include information for only those VOCs that were indicated to be present from the DSITMS data. It is possible that the DSITMS results may include false negatives, which in this context would be defined as the non-detection of a VOC when it was actually present in the sample

above the DSITMS detection limits. Estimating the concentrations from the DSITMS analyses proved to be difficult if not impossible in many cases. This can be attributed to several reasons which include the lack of pure chemicals to prepare gas standards of the tentatively identified VOCs (i.e., sulfur hexafluoride and perfluoropropane), overlapping quan ions for tentatively identified VOCs (i.e., m/z 91 was the base peak for toluene, ethylbenzene, and the xylenes; and m/z 69 was the base peak for perfluoropropane and perfluoro-1,3-dimethyl-cyclohexane), and/or ion counts that were too low to permit accurate quantitation (due to concentrations in the Mir samples taken for DSITMS analysis being so close to the DSITMS detection limits as discussed above). Nevertheless, quantitation was attempted in some cases, and here DSITMS concentrations were compared to the GC/MS results where available. The GC/MS concentrations reported in these tables were converted to units of ppb and corrected to include the dilution factors so as to reflect the concentrations of each VOC in the samples taken for DSITMS analysis. This was deemed to be more appropriate than the reverse scenario (i.e., reporting DSITMS results in the Mir atmosphere in units of mg/m^3) as the ppb units illustrate how low the concentrations were in the samples analyzed and how close they were to the approximately 10-50 ppb DSITMS detection limits.

Mir 21 samples were not analyzed via DSITMS, as almost the entire volume of each sample was used for GC/MS analyses. Subsequent GC/MS analyses of Mir 22 samples utilized smaller sample volumes and the samples were then repressurized to provide reasonable sample volumes for DSITMS analyses. DSITMS results from samples AA01466, AA01467, AA01657, AA01613, AA01661, and AA01617 are summarized in Tables 20-25. These represented the first DSITMS analyses of Mir samples. Of interest is the detection of sulfur hexafluoride as indicated by the presence of a relatively intense ion at m/z 127 in samples AA01466 and AA01467. It should be noted that this particular compound was detected at relatively high concentrations by GC/MS analyses of Mir 21 GSC samples AA01241 and AA01243, but not in later GSC samples, most likely due to the fact that it was not trapped efficiently by the air concentrator. This illustrates an important advantage of DSITMS versus GC/MS: the ability to detect permanent gases that would not normally be separated or detected by a GC/MS method that was by necessity tailored for VOCs. Perfluoro-1,3-dimethyl-cyclohexane was clearly indicated in samples AA01466, AA01467, AA01657, and AA01613 by the presence of ions at m/z 69, 181, 131, and 100. Toluene and ethylbenzene/xylenes were detected in samples AA01657, AA01613, AA01661, and AA01617 as indicated by the presence of ions at m/z 91 and 92 for toluene and m/z 91 and 106 for ethylbenzene and the xylene isomers. Hexamethylcyclotrisiloxane was indicated in samples AA01466, AA01657, AA01613, AA01661, and AA01617 by the presence of an ion at m/z 207, although no other characteristic ions for this compound were observed in the mass spectra. It should be noted that although octamethylcyclotetrasiloxane was present in these samples as indicated by the GC/MS data, the m/z 220 limit of the scan range in these DSITMS analyses precluded detection of the base peak at m/z 281 for this VOC. Quantitation was not attempted for any of these VOCs due to either the lack of gas standards (sulfur hexafluoride and hexamethylcyclotrisiloxane), overlapping quan ions (m/z 91 for toluene and ethylbenzene/xylenes), and/or low ion intensities.

Mir 23 samples were analyzed via DSITMS, and the results from samples AA01761, AA01797, AA01815, and AA01811 are summarized in Tables 26-29. The results are similar to those presented above for the Mir 22 samples, although some quantitative information is reported. Sulfur hexafluoride was detected in samples AA01761 and AA01797. Dichlorodifluoromethane and trichlorofluoromethane were detected in sample AA01761. Perfluoropropane and perfluoro-1,3-dimethyl-cyclohexane were indicated in samples AA01761 and AA01797. Benzene was indicated in sample AA01811; toluene in samples AA01797, AA01815, and AA01811; and ethylbenzene/xylenes in all 4 samples. Octamethylcyclotetrasiloxane was indicated in samples AA01797, AA01815, and AA01811. Gas standards for sulfur hexafluoride, perfluoropropane, and hexamethylcyclotrisiloxane were not available and hence quantitation was not attempted for these compounds. Although gas standards were available for both dichlorodifluoromethane and trichlorofluoromethane, these were not run due to operator oversight. Four-point calibration curves for perfluoro-1,3-dimethyl-cyclohexane, benzene, toluene, o-xylene, and octamethylcyclotetrasiloxane were

generated using gas standards prepared and analyzed on the same day as the samples. In some cases, the quan ion counts in the samples were too low to permit accurate quantitation. This is further supported by the accompanying GC/MS data, which were corrected for the dilution factors to show the concentration of each VOC in the samples analyzed via DSITMS, and are close to the ~10-50 ppb DSITMS detection limits. Two notable exceptions are samples AA01815 and AA01811, which were collected shortly after the fire event. Both samples show elevated levels of benzene, toluene, and ethylbenzene/xylenes, most likely since these were produced as products of incomplete combustion. The reported DSITMS concentrations for toluene and xylenes are lower than the corresponding GC/MS concentrations by more than an order of magnitude, most likely due to the nonspecific means used for quantitation. The DSITMS concentrations for octamethylcyclotetrasiloxane agree quite well.

Mir 24 samples were analyzed via DSITMS, and the results from samples AA02093, AA02094, AA02113, AA02104, AA02114, and AA02107 are summarized in Tables 30-35. The results are similar to those presented above, but once again only limited quantitative information is reported. No GC/MS results were available for intercomparison as these samples were preserved exclusively for DSITMS experiments. However, these results can be compared against those GC/MS from the JSCC Toxicology lab. DSITMS analyses again indicated the presence of sulfur hexafluoride, fluorocarbons, aromatic hydrocarbons, and siloxanes in the samples. Gas standards for sulfur hexafluoride, perfluoropropane, and hexamethylcyclotrisiloxane were not available and hence quantitation was not attempted for these compounds. Although gas standards were available for octamethylcyclotetrasiloxane, these were not run due to operator oversight. Four-point calibration curves for perfluoro-1,3-dimethyl-cyclohexane, benzene, toluene, and o-xylene were generated using gas standards prepared and analyzed on the same day as the samples. A corrective method was employed in an attempt to derive quantitative information for both perfluoropropane and perfluoro-1,3-dimethyl-cyclohexane in these samples. The concentration of perfluoropropane was estimated by the response of the unique quan ion at m/z 119. The concentration of perfluoro-1,3-dimethyl-cyclohexane could not be determined directly as this compound did not provide a unique quan ion in the samples, and hence its concentration was computed by subtracting out the estimated contribution of perfluoropropane to m/z 69. Although the calculated concentrations are reported in these tables, it is highly likely that this means of quantitation is highly imprecise.

The DSITMS analyses of the Mir samples represent a “best effort” basis using methods that were continually under development over the course of this investigation. The qualitative results show consistent detection of VOCs known to be present at relatively high concentrations on Mir. The quantitative results are less reliable due to limited sample volumes, low sample concentrations, and experimental compromises. Although DSITMS results can be compared against those from the more widely accepted GC/MS techniques, some caveats must be noted here. The samples taken for analysis via DSITMS were not the same as those used for GC/MS as they were repressurized and then analyzed months later due to the logistics of transferring the samples to the investigators’ labs. A more valid and worthwhile comparison between the two techniques, which was not effected over the course of this investigation, would utilize identical samples for both DSITMS and GC/MS analyses and involve the analysis of more complex samples containing several gas standards at concentrations that exceed the 10-50 ppb DSITMS detection limits.

The bulk of the efforts associated with this project went into the research and development of new DSITMS techniques. This involved a high school student, numerous undergraduate students, and two graduate students who eventually went on to receive their master’s degrees. Some of these results are reported in detail elsewhere in the various publications, conference proceedings, and presentations associated with this project. A full listing of these references are provided in the NASA task bibliography. A brief review of these research and development efforts is given here to provide some context for evaluating the performance of the DSITMS technique; to illustrate its inherent flexibility, advantages, and disadvantages; and to point out its utility not only for life support monitoring but other Earth-based applications as well [4].

A basic schematic of the DSITMS technique is shown in Figure 18. The major difference between DSITMS and the more conventional GC/MS technique used for the determination of VOCs in air include the lack of an air concentrator and GC. This has several implications with respect to the analytical performance. Sensitivity will necessarily be reduced, as only small sample volumes can be accommodated into the DSITMS instrument so as to not compromise the vacuum system, compared to the typically 100 mL and larger volumes typically employed in GC/MS analyses. Some of this sensitivity loss can be made up by the inherent sensitivity of the ion trap and its ability to selectively store ions. Selectivity will also be reduced, as the entire sample will be enter the trap at one time, compared to the usual one sample every few seconds due to the highly efficient separations provided by high resolution capillary GC columns. This loss of selectivity can be recovered somewhat through the ability of the ion trap to selectively store and fragment ions in the techniques referred to as selected ion monitoring (SIM) and tandem mass spectrometry (MS/MS). The main advantage of DSITMS over GC/MS is the vastly reduced analysis times, which are on the order of a second per analyte versus the typical 40 minutes or longer for GC/MS. Additional advantages provided by DSITMS include the relatively small size, simpler hardware, lower cost, and fewer possible points for failure.

DSITMS can accommodate a number of different sample introduction systems. Some of the inlet systems studied over the course of this work are shown in Figures 1, 2, 19, and 20. Schematics of the two versions of the real-time air monitor (RTAM) device used in for Mir sample analyses and generation of cal curves are given in Figures 1 and 2. Both devices are relatively simple to tune and operate. They function by mixing the sample with a stream of helium, which normally serves as a buffer gas for the ion trap. The resulting stream is passed through an open-split interface, where 99% is pumped away, allowing only a small portion into the ion trap, hence reduced response times. It should be noted that the newer version of the RTAM device allows the sample flowrate to be lowered without compromising sensitivity. This was particularly useful in extending the analysis times for the Mir 24 samples. A membrane inlet developed and studied in the course of this investigation is shown in Figure 19 [36]. This device uses a membrane to selectively concentrate VOCs from an air stream into a helium stream, and a jet separator to provide a second stage of enrichment, prior to introduction into the ion trap. The advantages of this inlet include lower detection limits. Its disadvantages include response and recovery times on the order of minutes and poor response to more polar VOCs. Finally, a glow discharge source shown in Figure 20 was briefly studied [37]. This device theoretically offers perhaps the best sensitivity, as the sample is ionized external to the ion trap, and the resulting ions are then injected into and stored in the ion trap for subsequent mass analysis. Physical separation of the region of ionization from mass analysis allow for more sample to be ionized without compromising the vacuum system of the ion trap, hence lowering detection limits. This device also enables the generation and sampling of either positive or negative ions, which is not normally possible with internal ionization ion traps. This is attractive insofar that negative ion mode would be more selective and sensitive for fluorinated and chlorinated hydrocarbons, while positive ion mode would be used for hydrocarbons.

The ion trap also accommodates the use of a variety of ionization modes, including electron ionization (EI) and chemical ionization (CI). However, the ionization modes accessible are a function of the inlet system deployed. Experimental work over the course of this investigation has shown that charge exchange ionization is the dominant ionization mode when the RTAM is employed and large amounts of air enter the ion trap [14,22,38]. EI provides abundant fragment ions, whereas CI is a softer ionization technique and can provide larger molecular ion intensities. This is particular important for MS/MS scan modes as will be discussed below.

The ion trap can accommodate MS, SIM, MS/MS, and MSⁿ scan modes, each providing greater selectivity than the former. MS scan mode was used in the DSITMS analyses of Mir samples. This enabled the screening for a wide range of VOCs in a one scan. SIM would provide more precise quantitation for a tentatively identified target VOC from an MS mode analysis. MS/MS and MSⁿ would provide more

definitive identification and more reliable quantitation. The greater selectivity inherent to MS/MS is a function of selecting a parent or precursor ion, and then fragmenting that ion to produce a characteristic daughter or product ion. The chances of another compound having the same precursor-product ion combination is small but not impossible. Many structural isomers, such as ethylbenzene and xylenes, or monoterpenes [39] have near identical fragmentation patterns that do not permit their differentiation. Given the similar SMACs for these compounds, it is unclear as to whether a selective technique for each of these isomers is required or whether a total measurement of all isomers would suffice. The key to more sensitive MS/MS analyses is using CI to concentrate the signal for a target VOC into predominantly one ion for subsequent MS/MS analyses. In this work, the inability to provide more selective identification and quantitation of target VOCs was largely a function of the use of EI, which provided more extensive fragmentation and far too low intensities of the more characteristic, heavier mass ions. Although CI was evaluated and tested as part of this investigation, the design features of the ion trap instrument used in this work provided poor sensitivity in CI mode, most likely due to the positioning of the CI gas inlet in close proximity to the turbo pump.

A great deal of data was generated over the course of this project highlighting the ability of DSITMS to provide sensitive and selective detection of trace levels of VOCs in air. Calibration curves were generated for perfluorinated hydrocarbons [35], chlorofluorocarbons [22,40], aromatic hydrocarbons [41], terpenes [42], and siloxanes. While presentation of all of this data here is beyond the scope of this report, some data are presented here to illustrate the utility and specifics of the DSITMS technique. An illustration of the sensitivity and selectivity of DSITMS are provided in Figure 21. In this case, the RTAM inlet was challenged with zero grade air followed by increasing concentrations of gas standards containing benzene, toluene, and xylene in air. The top two plots show total and selected ion chromatograms, and the bottom plot shows a background subtracted mass spectrum which clearly indicates that 10 ppb levels of benzene, toluene, and o-xylene is possible. An illustration of the linearity of detection and sensitivity-selectivity tradeoff inherent to DSITMS is shown in Figure 22. This plots DSITMS calibration curves for benzene, toluene, and o-xylene in MS and MS/MS modes. MS mode provides the poorest selectivity, as the presence of one ion may not be unique to the target compound in question. MS/MS mode provides greater selectivity by isolating the ion of interest and then monitoring the intensity of a characteristic fragment ion, but the detection limits may not as good as MS mode because a less intense and more unique precursor ion was chosen and/or the fragmentation efficiency of the precursor ion may not be 100%. The use of CI would alleviate some of these problems as described above.

A brief summary of the strengths and weaknesses of DSITMS are provided below.

Sensitivity:

- The detection limits of the DSITMS technique are ~10-50 ppb in MS, SIM, and MS/MS modes (note detection limits may be higher in MS/MS mode depending on fragmentation efficiency of the particular precursor ion in question).
- These detection limits meet the required detection limits for space applications for even the more toxic VOCs (i.e., can detect benzene at ~50 ppb, which is below detection limit of $1/10^{\text{th}}$ of 7-day SMAC or 47 ppb).
- These detection limits are not sensitive enough to monitor *ambient* levels of many VOCs (note that these concentrations of many VOCs are well below the detection limit of even GC/MS).

Selectivity:

- DSITMS can address blind spots in GC/MS analyses insofar that that can be used to detect permanent gases as well as VOCs (i.e., DSITMS showed detection of SF₆ and other permanent gases which were not detected using conventional GC/MS methods for VOCs in air).

- DSITMS poses a selectivity-sensitivity tradeoff (can increase sensitivity at expense of selectivity by using SIM or MS mode, and vice versa).
- DSITMS may not be able to differentiate between structural isomers (i.e., DSITMS cannot distinguish between ethylbenzene and various xylene isomers).
- DSITMS cannot easily detect low molecular weight species such as formaldehyde (this molecule has a quaternary ion that overlaps major ions from air).
- DSITMS is a better alternative to GC/MS for screening for VOCs in a life support environment, although GC/MS is a better alternative for providing more definitive analyses of complex, uncharacterized mixtures of VOCs in air (a little chromatography goes a long way).

Speed:

- DSITMS provides near instantaneous response to specific VOCs, and hence can be used to follow rapid changes in VOC concentrations versus time.
- DSITMS for life support monitoring would minimize time between sampling and analysis and hence reduce potential sources of error.

Simplicity:

- DSITMS requires simpler hardware and operator expertise versus GC/MS.
- DSITMS can be deployed without the use of helium as a buffer gas [22], which would certainly be desirable for space deployment.
- A prototype field-portable DSITMS instrument was developed but never brought to market [45]. Future commercial efforts towards this end should be monitored.

Conclusions

GC/MS analyses of the Mir samples met the expected performance requirements. Results showed common VOCs normally found in air samples, including halogenated hydrocarbons, aromatic hydrocarbons, aliphatic and cyclic hydrocarbons, oxygenated hydrocarbons, and siloxanes. All of these VOCs were present at concentrations several orders of magnitude below their SMACs. Further comments on the toxicological significance of the data are not provided here, are beyond the scope of this investigation, and are the focus of ongoing efforts at the JSC Toxicology Lab.

DSITMS analyses of the Mir samples, although limited in scope, were likewise successful and identified VOCs present at concentrations exceeding the 10-50 ppb detection limit. It should be noted that the DSITMS results did not indicate any false positives (identifying a VOC that was not indicated in GC/MS data). Furthermore, DSITMS was shown to be capable of monitoring permanent gases as well as VOCs, which is a “blind spot” in GC/MS analyses. The technique has potential for use in such diverse Earth-based applications such as stack monitoring, fence-post monitoring, air quality monitoring, breath analysis, and explosives detection [44]. In fact, the DSITMS method has been formalized into a draft EPA method for screening to screen for VOCs in air, water, and soil matrices [46]. Although the technique at this point is not mature enough to deploy for life support monitoring applications, it shows great promise and with continued evolution of this technology should eventually enjoy wider applications both on Earth and in space.

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